

# PATENT SPECIFICATION

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## (54) TREATMENT OF RUBBER

(71) We, THE BOARD OF THE RUBBER RESEARCH INSTITUTE OF MALAYSIA, a Malaysian body Corporate, of 260 Jalan Ampang, P.O. Box 150, Kuala Lumpur, Malaysia, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement—

Viscosity-stabilised (CV) natural rubber does not normally require mastication prior to mixing operations in a consumer factory. The attendant cost savings accrued from this special feature is the principal attraction of viscosity-stabilised rubbers. Commercially rubber has been stabilised by the addition of hydroxylamine to latex (British Patent No. 965,757). In certain applications, however, the dark colour and slow curing characteristics of CV rubbers made using hydroxylamine and now available are not acceptable. To widen its acceptability, a CV grade with light colour and fast curing characteristics is desirable.

The present invention accordingly provides a method of stabilising the viscosity of natural rubber, which method comprises adding to fresh solid natural rubber an effective amount of semicarbazide or an acid addition salt thereof.

By the term "fresh solid natural rubber" we mean solid natural rubber which has undergone substantially no storage hardening. Storage hardening or loss of plasticity on storage of natural rubber occurs progressively in the rubber after tapping. Under normal treatment the degree of storage hardening during coagulation and subsequent treatment on the rubber plantation is not substantial. The prolonged storage e.g. during transportation and warehousing, which generally occurs before the rubber is used in industrial manufacture, results in extensive hardening of the rubber which cannot be dealt with satisfactorily by subsequent treatment with semicarbazide. The present invention is restricted to treatment of natural rubber before such extensive hardening occurs.

The form of semicarbazide used is not critical; the free base or acid addition salts may

be utilized as solids or in suspension or solution for example in water. From its ready availability and convenience in handling semicarbazide hydrochloride is preferred. Neutral acid addition salts have the advantage that the pH change resulting from the addition to rubber is minimised.

The minimum quantity of semicarbazide necessary to effect useful viscosity stabilisation is not known precisely. Quantities of as little as 0.02% by weight of semicarbazide based on the weight of rubber treated can provide a useful degree of stabilisation. Conventionally viscosity stabilised rubber i.e. CV rubber has been defined as rubber which increases its viscosity by not more than 6 Mooney units on accelerated storage hardening under specified conditions. The precise quantities of semicarbazide actually incorporated into the rubber are rather difficult to assess because of spillage loss etc. The preferred figures thus relate to the total quantity of semicarbazide consumed (including spillage loss). To achieve this level of stabilisation it would be usual to add at least 0.1% by weight of semicarbazide and preferably at least 0.2%. The upper limit of addition is governed by increasing cost balanced against diminishing returns. A practical maximum of 0.5% by weight is reasonable and it would be usual to have a maximum of 0.3% by weight. The high cost of semicarbazide as compared with hydroxylamine at the present time favours relatively low levels of addition in order to improve the economics of the present process.

The semicarbazide can be added at any convenient times during processing of the rubber, e.g. by dipping rubber crumb in a solution containing semicarbazide, by adding semicarbazide to dry coagula and by adding semicarbazide to wet coagula. The invention is applicable to smoked or unsmoked rubber, crepe rubber, solid rubber from latex (preferably suitably preserved latex), cuplumps and compounded or uncompounded rubber provided that the rubber has undergone substantially no storage hardening. It is preferable that the addition of semicarbazide should be made as early as possible. It follows from this that, in the case of rubbers from latex, the

latex should not be stored for a long period before coagulation as storage hardening may occur in the latex.

In a preferred aspect the invention provides a method of treating natural rubber to provide viscosity stabilisation which method comprises contacting crumb rubber with an aqueous solution of semicarbazide or an acid addition salt thereof. This method is preferred because it is normal procedure to produce crumbs of solid rubber during the coagulation and manufacture of solid natural rubber. A particularly preferred way of doing this is to dip wet latex crumbs as prepared in normal rubber production into an aqueous solution of semicarbazide hydrochloride. During dipping some of the semicarbazide in the solution is absorbed by the rubber and is distributed homogeneously throughout the rubber during subsequent processing. It is usual for wet latex crumbs to be dried by heating to remove excess moisture.

We have found that wet crumb rubber briefly (less than 1 minute) dipped in 1.2% by wt. aqueous semicarbazide hydrochloride solution absorbs 0.17 to 0.20 parts by weight of semicarbazide hydrochloride per 100 parts by wt. of dry rubber.

In the accompanying drawing,

Figure 1 shows the dependence of dipping time of wet crumb rubber on the concentration of semicarbazide hydrochloride solution, the drying temperature being 110° C.

Figure 2 shows the effect of drying temperature, and

Figure 3 shows the extent to which various forms of solid rubber are viscosity stabilised by being dipped in semicarbazide hydrochloride solution.

For effective viscosity-stabilisation of the rubber, the duration of dipping is inversely related to the strength of the dipping solution (Figure 1). For practical reasons, the dipping of crumbs for a relatively short duration, e.g. less than 1 minute in a relatively strong semicarbazide hydrochloride solution is preferred because it can provide the basis of a continuous process which lends itself to automation. Loss of chemical through spillage can be minimised with a suitable design of equipment. We believe that the aqueous solution should contain at least 0.3% by weight of semicarbazide hydrochloride. Though a 0.6% by wt. solution is sufficient for viscosity-stabilisation to the CV criterion using a brief dip (Figure 2), a 1.2±0.1% by wt. solution is recommended for large scale production. This allows for a sufficient safety margin in processing, variation in crumb size in commercial production and variation in drying conditions. More concentrated solutions up to 2% by wt. or more can be used, but do not provide any very great advantage over 1.2% by wt. solutions.

In this dipping process, semicarbazide hydrochloride remains on the surface of the crumbs and therefore is subjected to drastic

heat treatment. Hence, the drying temperature is an important factor in the preparation of light-coloured CV rubber. For effective stabilisation, crumbs dried at 120° C require a higher concentration of semicarbazide hydrochloride solution than crumbs dried at 100° C (Figure 2). This could be attributed to the slight heat instability of semicarbazide hydrochloride which has a decomposition temperature of 173° C. Since a high drying temperature gives a dark rubber it is advisable to dry the crumbs at a temperature not exceeding 110° C.

Another way to include the semicarbazide is to add it to dry rubber. This can be conveniently performed by mixing dry rubber with semicarbazide hydrochloride in a 2 roll-mill, an internal mixer (e.g. a Banbury mixer) or in some other mixing apparatus. Semicarbazide may be in the dry form but more preferably in the form of a rubber masterbatch.

A further way to effect incorporation is to add semicarbazide to wet coagula. This can be conveniently performed during creping. Semicarbazide may be added in the dry form or as a solution, e.g. a 20% by wt. aqueous solution of semicarbazide hydrochloride or preferably as a latex coagula masterbatch.

The temperature at which the rubber is treated with the semicarbazide is not critical. It is usually convenient to perform the treatment at or about ambient temperature. However, it is possible to perform the treatment at temperatures up to 100° C (i.e. the boiling point of the solution of semicarbazide). Wet coagula are conveniently treated at ambient temperature or at a slightly elevated temperature (3-6° C about ambient) generally generated during the creping operation. There is, however, no reason why the treated rubber should not be heated at a temperature up to 60° C during creping.

The pH of treatment is not critical and is conveniently governed by the pH of the form of semicarbazide used. However, as is mentioned above, neutral salts are preferred to minimise changes in pH.

The following examples illustrate the manner in which the invention may be carried out.

#### EXAMPLE 1.

Field latex was treated with 0.7% by wt. castor oil and 0.04% by wt. sodium metabisulphite (based on the dry rubber content (DRC) of the latex). This was coagulated with 2% w/v formic acid at pH 5.0. The coagulum was matured for 16 hours before it was passed through the crumblers. The crumbs were dipped in a 1.2% by wt. aqueous solution of semicarbazide hydrochloride. This was followed by drying the treated crumbs at 110° C for 4 hours.

SMR 5L rubber and hydroxyamine CV rubber (SMR 5CV) were prepared from the

same lot of field latex by the conventional process.

The new rubber properties are given in Table 1 while the vulcanisate properties together with details of formulation used, mixing and vulcanisation conditions are given in Tables 2 and 3.

#### EXAMPLE 2.

A dry SMR 5L rubber was mixed with 0.0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, and 0.50 p.h.r. semicarbazide hydrochloride on a two roll-mill. The mixing time was 4 minutes at the roll starting temperature of 40, 70 and 100° C. Semicarbazide hydrochloride was added in the dry form.

Details of the samples and the test results are given in Table 4.

It is evident from the results that the addition of semicarbazide prevented the rubber from hardening.

#### EXAMPLE 3.

A dry SMR 5L rubber was mixed with 0.0, 0.05, 0.10, 0.15, 0.20, 0.30 and 0.50 p.h.r. semicarbazide hydrochloride in a Banbury (OGC model, rotor speed 80 rpm) for 2 and 2 minutes mixing time at two rotor/jacket starting temperature of 100° C and 120° C. Semicarbazide hydrochloride was added in the form of a 50:50 semicarbazide hydrochloride: SMR 5L master batch together with the rubber samples at the start of the mixing cycles.

Details of mixing and the test results are given in Table 5.

It is evident from the results that the addition of semicarbazide prevents the rubber from

hardening but it stabilises the viscosity at a higher level.

(2) Semicarbazide CV rubber whose properties are set out in Tables 1-3 was prepared as follows:—

As shown in Table 1, semicarbazide hydrochloride CV rubber is lighter in colour and faster curing than the hydroxylamine CV rubber and is comparable to the (unstabilised) corresponding SMR 5L in these properties. Semicarbazide hydrochloride CV rubber is approximately 5 Mooney units higher than the hydroxylamine CV rubber. This feature could be of advantage to factories which can only produce CV 55 instead of CV.

Slight differences in the physical properties of the ACS 1 vulcanisates are attributed to differences in their cure behaviour. In general, the vulcanisate properties of semicarbazide hydrochloride CV rubber in practical compounds are comparable to those of hydroxylamine CV rubber and SMR 5L (Tables 2 and 3).

The economic manufacture of a CV rubber with colour and cure rate comparable to SMR 5L is thus possible. This involves the dipping of crumbs from normal SMR 5L production in an aqueous solution of semicarbazide hydrochloride before drying. This treatment can be easily incorporated in the flow line of new process SMR factories. No major development work is necessary.

The process also provides a convenient method for viscosity stabilising of cuplumps and unsmoked sheets (Figure 3) and has been successfully adopted in the production of viscosity-stabilised tyre rubber.

TABLE 1

Raw Rubber Properties

Properties	Semicarbazide Hydrochloride CV Rubber	Hydroxylamine CV Rubber	SMR 5L
Dirty (% wt.)	0.01	0.01	0.01
Ash (% wt.)	0.22	0.18	0.20
Nitrogen (% wt.)	0.43	0.40	0.41
Volatile Matter (% wt.)	0.30	0.30	0.31
Mooney Viscosity ML 1 + 4' at 100°C	59	54	65
ΔVR	4	4	17
PRI	83	87	85
Colour (Lovibond Units)	4.0	6.5	3.5
Mod Value	6.0	5.4	5.9
P <sub>0</sub>	41	39	46

TABLE 2

## ACS-1 Mix Vulcanisate Properties

Compound Formulations (parts by weight)

Rubber	100
ZnO	6
Stearic Acid	0.5
MBT	0.5
S	3.5

Properties	Cure Time at 140°C	Semicarbazide Hydrochloride CV Rubber	Hydroxylamine CV Rubber	SMR 5L
Tensile Strength (MN.m <sup>-2</sup> )	30	21.1	17.4	21.5
	40	24.0	14.7	23.1
	50	20.3	18.1	22.6
Elongation at Break (%)	30	820.0	810.0	790.0
	40	820.0	780.0	800.0
	50	790.0	800.0	790.0
Modulus at 300% (MN.m <sup>-2</sup> )	30	0.9	0.9	1.1
	40	1.4	1.0	1.4
	50	1.4	1.1	1.4
Modulus at 600% (MN.m <sup>-2</sup> )	30	5.3	5.0	6.3
	40	6.6	4.7	6.5
	50	6.6	5.0	6.5
Relaxed Modulus MR100 (MN.m <sup>-2</sup> )	30	0.6	0.5	0.6
	40	0.6	0.5	0.6
	50	0.6	0.5	0.6
Dunlop Resilience at 20°C (%)	30	83.9	78.8	84.3
	40	84.5	79.9	84.5
	50	84.5	80.3	84.5
Hardness (IRHD)	30	34.8	32.3	34.1
	40	35.3	33.0	35.1
	50	35.9	33.2	35.7

TABLE 2 (Continued)

Properties (40°/140°C Cure)	Ageing Conditions	Semicarbazide Hydrochloride CV Rubber	Hydroxylamine CV Rubber	SMR SL
Tensile Strength (MN.m <sup>-2</sup> )	7d/70°C	25.6 (107)	24.4 (166)	23.6 (102)
	14d/70°C	16.1 ( 67)	16.8 (114)	14.2 ( 61)
Elongation at Break (%)	7d/70°C	710 ( 87)	740 ( 95)	680 ( 85)
	14d/70°C	590 ( 72)	610 ( 78)	570 ( 71)
Modulus at 300% (MN.m <sup>-2</sup> )	7d/70°C	2.1 (150)	1.8 (180)	1.7 (121)
	14d/70°C	2.2 (157)	1.9 (200)	2.2 (157)
Modulus at 600% (MN.m <sup>-2</sup> )	7d/70°C	13.8 (209)	11.1 (236)	13.6 (210)
	14d/70°C	17.1 (259)	15.1 (321)	—
Relaxed Modulus MR100 (MN.m <sup>-2</sup> )	7d/70°C	0.7 (117)	0.7 (140)	0.7 (117)
	14d/70°C	0.7 (117)	0.7 (140)	0.7 (117)

Figures in brackets denote % retention after ageing

TABLE 3

Tread Mix - Vulcanisate Properties  
Compound Formulations (Parts by weight)

NR	100
ZnO	4
Stearic acid	2
HAF	50
Dutrex R	5
Nonox ZA	1.5
Nonox BL	1.0
Santocure NS	0.5
S	2.5

Properties (45' at 140°C Cure)	Ageing Conditions	Semicarbazide Hydrochloride CV Rubber	Hydroxylamine CV Rubber	SMR 5L
Tensile Strength (NM.m <sup>2</sup> )	Unaged	28.1	27.4	28.0
	1d/100°C	19.7 (70)	21.1 (77)	20.6 (74)
	3d/100°C	8.2 (29)	8.7 (32)	7.5 (27)
Elongation at Break (%)	Unaged	520	510	510
	1d/100°C	350 (67)	370 (73)	340 (67)
	3d/100°C	180 (35)	180 (35)	150 (29)
Modulus at 300% (MN.m <sup>2</sup> )	Unaged	13.4	13.5	13.6
	1d/100°C	17.2 (128)	17.3 (128)	18.4 (135)
Relaxed Modulus MR100 (MN.m <sup>2</sup> )		2.08	2.04	2.10
Dunlop Resilience at 20°C (%)		62.3	61.9	62.4
Hardness (IRHD)		67.0	65.7	65.9
Tear Strength (N per std. test piece)		359.4	319.9	330.6
Akron Abrasion Dusted (ml. loss/1,000 rev.)		0.066	0.062	0.062
Flex cracking (Kcs. to Grade C)		90	90	120
		100	110	110

The words "Dutrex", "Nonox" and "Santocure" are Registered Trade Marks.

TABLE 3 (Continued)

Properties (45° at 140°C Cure)	Ageing Conditions	Semicarbazide Hydrochloride CV Rubber	Hydroxylamine CV Rubber	SMR 5L
Cut Growth 2-4 min. (Kcs.)		3.00	2.60	2.25
4-8 „		10.00	9.70	7.80
8-12 „		35.33	11.30	11.15
Goodrich Flexometer (Heat build-up)				
Starting conditions      Stroke = 0.175"; Applied Load = 30 lbs.				
Temperature (°C) rise after 25 min.		37	34	32
Temperature (°C) rise after 60 min.		48	48	44
Permanent Set (%)		17.1	17.9	16.2
Dynamic Compression Set (%)		13.4	14.5	12.1
Relative Resilience (%)		66.7	63.8	67.0
Compression Set (%) (72 hrs. at 20 ± 2°C) 30' rec.		8.0	8.1	8.1

Figures in brackets denote % retention after ageing

Other methods of adding the semicarbazide include those described in detail in British Patent specification No. 1,373,630 in connection with the treatment of solid rubber using hydroxylamine. These methods are in general applicable in the present invention by substituting semicarbazide or an acid addition salt thereof for the hydroxylamine used in the prior case.

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TABLE 4

Viscosity Stabilisation of Dried Rubber with a Two Roll-Mill

Note: Mixing Time 4 Minutes

Sample	% Semicarbazide Hydrochloride (on Rubber)	Mixing Temp. °C	Mooney Viscosity (ML 1+4 at 100°C)	VR	PRI
1	0.00	40	36	14½	78.3
2	0.05	40	34½	15	79.8
3	0.10	40	34	10½	77.6
4	0.15	40	34½	5½	75.6
5	0.20	40	39	5	72.9
6	0.30	40	35	2	75.3
7	0.40	40	34½	3½	72.0
8	0.50	40	34½	½	72.5
9	0.00	70	55½	13¾	84.2
10	0.05	70	50½	11	81.3
11	0.10	70	55	9¾	81.3
12	0.15	70	55½	6½	79.9
13	0.20	70	58½	5	76.6
14	0.30	70	58½	½	76.5
15	0.40	70	54½	2	74.9
16	0.50	70	56	3	73.8
17	0.00	100	71¾	10¾	84.7
18	0.05	100	70¼	7¾	84.6
19	0.10	100	69¾	9¼	85.1
20	0.15	100	68¼	8	84.4
21	0.20	100	69¼	5½	78.2
22	0.30	100	68¾	3	78.5
23	0.40	100	67¾	3	78.8
24	0.50	100	69¼	2	79.6

TABLE 5

Viscosity Stabilisation of Natural Rubber with a Banbury

Sample	% Semicarbazide Hydrochloride (on Rubber)	Rotor & Jacket Temp. °C	Mixing Time (Mins)	Dump Temp. °C	Mooney Viscosity ML 1+4' at 100°C	VR	PRI
1	0.00	100	2	156	75½	15½	90
2	0.05	100	2	160	80½	3	85
3	0.10	100	2	159	83	2½	80
4	0.15	100	2	157	83	4	75
5	0.20	100	2	157	83	5½	72
6	0.30	100	2	162	79	3	66
7	0.50	100	2	160	78½	2½	63
8	0.00	100	3	175	72¾	19¾	89
9	0.05	100	3	176	77	7½	82
10	0.10	100	3	176	89	4	74
11	0.15	100	3	178	89	5	72
12	0.20	100	3	180	88½	4½	56
13	0.30	100	3	177	86	5	56
14	0.50	100	3	180	85	4	50
15	0.00	120	3	>180	70¾	22¾	90
16	0.05	120	3	>180	73¾	8¾	83
17	0.10	120	3	>180	88	6	74
18	0.15	120	3	>180	91	3	66
19	0.20	120	3	>180	89	5½	55
20	0.30	120	3	>180	86	5½	45
21	0.50	120	3	>180	86	5	39

## WHAT WE CLAIM IS:—

1. A method of treating natural rubber to provide viscosity stabilisation which method comprises adding to fresh solid natural rubber, as hereinbefore defined, an effective amount of semicarbazide or an acid addition salt thereof.
2. A method as claimed in claim 1 wherein the amount of semicarbazide or acid addition salt thereof added to the rubber is from 0.02 to 0.5% by weight based on the weight of the rubber.
3. A method as claimed in claim 2 wherein

the amount of semicarbazide or addition salt thereof added to the rubber is from 0.1 to 0.3% by weight based on the weight of the rubber.

4. A method as claimed in any one of claims 1 to 3 wherein the acid addition salt is a neutral acid addition salt of semicarbazide.

5. A method as claimed in any one of claims 1 to 4 wherein crumb rubber is contacted with an aqueous solution of semicarbazide or an acid addition salt thereof.

6. A method as claimed in claim 5 wherein

the crumb rubber is dipped in the aqueous solution.

5 7. A method as claimed in claim 6 wherein the rubber is dipped for a period of less than 1 minute.

8. A method as claimed in any one of claims 5 to 7 wherein the aqueous solution contains from 0.3 to 2.0% by weight of semicarbazide acid addition salt thereof.

10 9. A method as claimed in claim 8 wherein the solution contains about 1.2% by weight of semicarbazide or acid addition salt thereof.

10. A method as claimed in any one of claims 1 to 4 wherein the rubber is treated in the form of dry coagula.

15 11. A method as claimed in any one of claims 1 to 4 wherein the rubber is treated in the form of wet coagula.

12. A method as claimed in either claim 10 or claim 11 wherein the semicarbazide or acid addition salt thereof in dry form is used.

13. A method as claimed in either claim 10

or claim 11 wherein the semicarbazide or acid addition salt thereof in the form of a latex coagula masterbatch is used.

14. A method as claimed in any one of claims 1 to 13 wherein the rubber is treated at a temperature of up to 60° C during creping.

15. A method as claimed in any one of claims 1 to 14 wherein subsequent to the addition of the semicarbazide or acid addition salt thereof to the rubber, the rubber is heated to a temperature not exceeding 120° C.

16. A method as claimed in any one of claims 1 to 15 and substantially as hereinbefore described in any one of the Examples, or with reference to and as illustrated in any one of the accompanying drawings.

17. Viscosity stabilized natural rubber whenever made by the method claimed in any one of claims 1 to 16.

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